

The nature of ancient organic matter in buried paleosol mineral horizons

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Understanding the mechanisms controlling soil and sediment carbon storage is crucial for determining how future disturbances will affect carbon fluxes to the atmosphere. This research integrates isotopic, spectroscopic, and geochemical techniques, as well as an understanding of sedimentary processes, to study the types of plant and microbially-derived compounds sequestered in Holocene loess deposits and the processes responsible for their long-term stabilization. Loess depositional sites accumulating over millennial time periods in the central Great Plains of the United States reveal a dark horizon at 6 m depth referred to as the Brady soil. This band visually resembles a typical surface humic mineral horizon, but with low C concentrations (< 1 %), in disproportion with its dark color [1]. Due to their depth and geographic extension, the Brady soil represents considerable C stocks. Bulk soil in the buried Brady soil horizon has narrow C:N ranges, likely representing microbial products. We are fractionating organic matter in buried and surface horizons by density and particle size to determine occlusion within aggregates and association with mineral surfaces. The distribution of C, radiocarbon-based mean residence times, and stable C and N isotopic composition between different fractions will provide insight into mechanisms of physical and chemical stabilization. The chemistry of reference plant materials (leaf and root litter) from modern day analogues of the former vegetation will be analyzed using ^{13}C -NMR and pyrolysis gas chromatography mass spectrometry to determine potential sources of the buried organic matter. Long-term depositional sites provide a unique opportunity to document changes in SOM chemistry and residence time with changes in climate and vegetative cover over long time scales of centuries to millennia.

[1] Feggestad *et al.* (2004) *Phys Geog* **25**, 170–190.

Sr isotope quantification of siderite, brine and AMD contribution to high TDS well discharges

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The ability to characterize and monitor the results of CO₂ sequestration in geologic formations will require sensitive geochemical tools to identify and track the interactions of low-pH waters with confining and reservoir rock, brine, and groundwater. An analogous situation exists in a number of abandoned gas wells near Tylersburg, Pennsylvania, that penetrate Paleozoic sedimentary formations and discharge sulfate-dominated high TDS water; some have >100 ppm iron. Potential processes include groundwater interaction with brines from natural gas-producing units; pyrite oxidation and acid generation related to local coal mining; and dissolution of diagenetic siderite (FeCO₃). To assess their relative contributions, geochemical and strontium isotopic analyses were carried out on gas well discharges, groundwater, brines, AMD seeps, and siderite from sedimentary strata.

Groundwaters from an unaffected aquifer have relatively low [Sr] and high $^{87}\text{Sr}/^{86}\text{Sr}$ (0.03 ppm; 0.7192) that likely reflect a radiogenic source of Sr from intercalated shales. $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of deeper Devonian brines range from 0.7170–0.7173. Gas well discharges (0.7156–0.7160) are significantly different and indicate an additional source. Water chemistry suggests that AMD (locally pH ~4.2) is a plausible source of sulfate, and dissolution of FeCO₃ exposed to acidic waters could supply the excess iron and explain the circumneutral pH of the discharges. $^{87}\text{Sr}/^{86}\text{Sr}$ (0.7100) of nodular siderite from strip-mined overburden does not match. However, the composition of siderite cement from deeper sandstone aquifers (0.7159–0.7162) strongly suggests acidic waters promoted dissolution of iron carbonate from this stratigraphic level; the resulting waters migrated through aquifers and into wells. These findings demonstrate that Sr isotopic ratios can be used to delineate brine and groundwater interactions within isotopically distinct stratigraphic units.